ATTACHMENT B2

STATISTICAL METHODS USED IN SAMPLING AND ANALYSIS

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STATISTICAL METHODS USED IN SAMPLING AND ANALYSIS

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ATTACHMENT B2

STATISTICAL METHODS USED IN SAMPLING AND ANALYSIS

Introduction

The Permittees shall require generator/storage sites (**sites**) to use the following statistical methods for sampling and analysis of TRU mixed waste which is managed, stored, or disposed at WIPP. These statistical methods include methods for selecting waste containers for visual inspection, selecting retrievably stored waste containers for totals analysis, setting the upper confidence limit, and control charting for newly generated waste stream sampling.

B2-1 Approach for Statistically Selecting Waste Containers for Visual Examination

As a Quality Control check on the radiographic examination of waste containers, a statistically selected portion of the certified waste containers must be opened and visually examined. The data from visual examination shall be used to verify the matrix parameter category, waste material parameter weights, and absence of prohibited items as identified in Attachment B, Section B-1C, as determined by radiography.

The data obtained from the visual examination shall also be used to determine, with acceptable confidence, the percentage of miscertified waste containers from the radiographic examination. Miscertified containers are those that radiography indicates meet the Waste Isolation Pilot Plant Waste Acceptance Criteria and Transuranic Package Transporter-II Authorized Methods for Payload Control but visual examination indicates do not meet these criteria.

Participating sites shall initially use an eleven-percent (11%) miscertification rate to calculate the number of waste containers that shall be visually examined until a site-specific miscertification rate has been established. Sites may establish a site-specific miscertification rate by characterizing a lot of no less than fifty containers in a single Summary Category Group at the initial 11% miscertification rate. The results of this initial characterization shall then serve as the site-specific miscertification rate until reassessed annually as described below.

The site-specific miscertification rate shall be applied initially to each Summary Category Group to determine the number of containers in that Summary Category Group requiring visual examination, as specified in Table B2-1. However, a Summary Category Group-specific miscertification rate shall be determined when either six months have passed since radiographic characterization commenced on a given Summary Category Group, or at least 50% of a given Summary Category Group has undergone radiographic characterization, whichever occurs first. The Summary Category Group shall then be subject to the visual examination requirements of this reevaluated Summary Category Group-specific miscertification rate to ensure that the entire Summary Category Group is appropriately characterized. Table B2-1 provides the number of waste containers per Summary Category Group that shall be visually examined for various miscertification rates and waste container population sizes using a hypergeometric sampling approach. Sites shall use a miscertification rate of 1% for any Summary Category Group-specific miscertification rate calculated to be less than 1%.

The site-specific miscertification rate shall be reassessed annually by calculating a drum-weighted average of all historic Summary Category Group-specific miscertification rates. Each Summary Category Group-specific miscertification rate shall be rounded off to the nearest integer value before being used to calculate the new site-specific miscertification rate. Sites shall use a miscertification rate of 1% for any site-specific miscertification rate calculated to be less than 1%.

Table B2-1 has been developed with the use of an EG&G Idaho, Inc. engineering design file (EG&G 1994). The number of waste containers requiring visual examination is based on a 90 percent confidence that the actual miscertification rate (for the population) is less than the 90 percent upper confidence level (**UCL**), and also an 80 percent confidence that the UCL will be less than 14 percent if the actual miscertification rate is the same as the targeted percent of miscertified waste containers (column heading of Table B2-1). Thus, there is only a 10 percent probability that the UCL will be below 14 percent in the case where the actual miscertification rate is 14 percent or greater. Also, there is only a 20 percent probability that the UCL will be above 14 percent in the case where the actual miscertification rate is the same as the targeted percent.

The hypergeometric approach to determining the number of containers to be visually examined is dependant upon the defined estimate of the allowable proportion of containers that were miscertified and information on previous percentages of containers that were miscertified. The rationale and details of this methodology are discussed below.

In a population of size N, there are M miscertified containers, so the true proportion of the miscertified containers in the population is $M/N = p_{true}$. Since p_{true} (or M) is not known, p_{true} shall be estimated by randomly sampling some of the containers. If in a sample of n containers, x are found to be miscertified, the sample estimate ($\hat{p}$) of the true population proportion p_{true} is:

$$\hat{p} = \frac{x}{n} \qquad \text{(B2-1)}$$

This value is only an estimate, and as a result has some uncertainty associated with it. This uncertainty shall be quantified by calculating the upper one-sided (1-a) percent confidence limit for p, defined as p_{UCL}. This confidence limit gives the largest value the true proportion could take on and still have a “reasonable” chance (e.g., an a = 0.10 probability) of producing x miscertified containers in a sample of n out of N. This upper confidence limit is calculated as:

$$p_{UCL} = \frac{M_{UCL}}{N} \qquad \text{(B2-2)}$$

where M_{UCL} is the smallest value of M such that the probability of observing x or fewer miscertified containers in a sample of size n is less than or equal to a. That is, it is the smallest value of M such that the following inequality is true:

$$\sum_{k=0}^{x} \frac{\binom{M}{k}\binom{N-M}{n-k}}{\binom{N}{n}} \le a \qquad \text{(B2-3)}$$

where each term in parentheses has the usual combinatorial interpretation. For example:

$$\binom{M}{k} = \frac{M!}{k!\,(M-k)!} \qquad \text{(B2-4)}$$

Each term in the sum in Equation B2-3 is the hypergeometric probability of observing k miscertified containers in a sample size n from a population of size N in which there are M miscertified containers (and hence the population proportion of miscertified containers is p =M/N). The value M_{UCL} is obtained by substituting different values for M into Equation B2-3 until the largest value satisfying the inequality is found.

Note that in Equation B2-3, the upper confidence limit is dependent on x, the number of miscertifications observed in the sample, as well as on n, the sample size. To obtain the required sample size, the values of x that are likely to be seen shall also need to be considered. Sample size that shall be visually examined shall be determined by setting a desired upper confidence limit value and then manipulating x and n in Equation B2-3.

B2-2 Approach for Selecting Waste Containers for Statistical Sampling

B2-2a Statistical Selection of Containers for Totals Analysis

The statistical approach for characterizing retrievably stored homogeneous solids and soil/gravel waste and repackaged or treated S3000 waste that the generator/storage site demonstrates is not suitable for control charting using sampling and analysis relies on using acceptable knowledge to segregate waste containers into relatively homogeneous waste streams. Using acceptable knowledge, generator/storage sites will classify the entire waste stream as hazardous or nonhazardous rather than individual waste containers. Individual waste containers serve as convenient units for characterizing the combined mass of waste from the waste stream of interest. Once segregated by waste stream, random selection and sampling of the waste containers followed by analysis of the waste samples shall be performed to ensure that the resulting mean contaminant concentration provides an unbiased representation of the true mean contaminant concentration for each waste stream. The Permittees shall require each site project manager to verify that the samples collected from within a waste stream were selected randomly.

An end use of analytical results for retrievably stored homogeneous solids and soil/gravel is for assigning the Environmental Protection Agency hazardous waste D-codes that apply to each mixed waste stream and to confirm acceptable knowledge. The D-codes are indicators that the waste exhibits the toxicity characteristic for specific contaminants under the Resource Conservation and Recovery Act (**RCRA**). The RCRA-toxicity determination is made on the basis of sampling and analysis of waste streams and on whether or not the waste stream includes F-code wastes. If a waste stream includes one or more RCRA F-codes identified via acceptable knowledge, toxicity characteristic contaminants associated with the F-code waste(s) are not included in the RCRA-toxicity characteristic determination. That is, the F-codes take precedence over RCRA-toxicity D-code, and the waste stream is assumed hazardous regardless of the concentration. Therefore, toxicity characteristics contaminants associated with F-codes(s) for a waste stream shall be omitted from all calculations for determining the number of containers to sample because these wastes streams are assumed to be hazardous. In addition, each toxicity characteristic contaminant associated with the F-code(s) shall be excluded from evaluation of analytical results to determine D-codes. Contaminants of interest for the sampling, analysis, and RCRA-toxicity determination of a waste stream, then, excludes contaminants associated with F-codes that have been assigned to the waste stream.

The sampling and analysis strategy is illustrated in Figure B2-1. Preliminary estimates of the mean concentration and variance of each RCRA regulated contaminant in the waste will be used to determine the number of waste containers to select for sampling and analysis. The preliminary estimates will be made by obtaining a preliminary number of samples from the waste stream or from previous sampling from the waste stream. Preliminary estimates will be based on samples from a minimum of 5 waste containers. Samples collected to establish preliminary estimates that are selected, sampled, and analyzed in accordance with applicable provisions of the WAP may be used as part of the required number of samples to be collected. The applicability of the preliminary estimates to the waste stream to be sampled shall be justified and documented. The preliminary estimates will be determined in accordance with the following equations:

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \qquad \text{(B2-5)}$$

$$s^2 = \frac{1}{n-1}\sum_{i=1}^{n} (x_i - \bar{x})^2 \qquad \text{(B2-6)}$$

where $\bar{x}$ is the calculated mean and s^2 is the calculated concentration variance, n is the number of samples analyzed, x_i is the concentration determined in the *ith* sample, and *i* is an index from 1 to n.

Based upon the preliminary estimates of x and s^2 for each chemical contaminant of concern, estimate the appropriate number of samples *(n)* to be collected for each contaminant using the following formulas from SW-846 (EPA 1996):

$$n = \frac{t^2_{\alpha,n_0-1} s^2}{(RT-\bar{x})^2} \qquad \text{(B2-7)}$$

Where:

n_0 = the initial number of samples used to calculate the preliminary sample estimate.
n = the calculated number of samples in the preliminary estimate.
t^2 = the 90th percentile for a t distribution with n_0-1 degrees of freedom.
RT = Regulatory Threshold of the contaminant (TC limit for toxicity characteristic wastes, PRQL for listed wastes)

The number of samples to be collected will be based upon the largest n calculated for each of the contaminants of concern. The actual number of samples collected shall be adjusted as necessary to ensure that an adequate number of samples are collected to allow for acceptable levels of completeness.

All calculations should be rounded up to the nearest integer. A minimum of five containers shall be sampled and analyzed in each waste stream. If there are fewer than the minimum or required number of containers in a waste stream, one or more containers shall be sampled more than once to obtain the samples of the waste. Otherwise any one container may be selected for sampling only once.

The calculated total number of required waste containers will then be randomly sampled and analyzed. Waste container samples from the preliminary mean and variance estimates may be counted as part of the total number of calculated required samples if and only if:

- There is documented evidence that the waste containers for the preliminary estimate samples were selected in the same random manner as is chosen for the required samples.

- There is documented evidence that the method of sample collection in the preliminary estimate samples were identical to the methodology to be employed for the required samples.

- There is documented evidence that the method of sample analysis in the preliminary estimate samples were identical to the analytical methodology employed for the required samples.

- There is documented evidence that the validation of the sample analyses in the preliminary estimate samples were comparable to the validation employed for the required samples. In addition, the validated samples results shall indicate that all sample results were valid according to the analytical methodology.

Upon collection and analysis of the preliminary samples, or at any time after the preliminary samples have been analyzed, the generator/storage site may assign hazardous waste codes to a waste stream. For waste streams with calculated upper confidence limits below the regulatory threshold, the site shall collect the required number of samples if the site intends to establish that the constituent is below the regulatory threshold.

B2-2b Statistical Selection of Containers for Headspace Gas Analysis

If a waste stream meets the conditions for representative headspace gas sampling in Permit Attachment B, Section B-3a(1), headspace gas sampling of that waste stream may be done on a randomly selected portion of containers in the waste stream. The minimum number of containers, *n*, that must be sampled is determined by taking an initial VOC sample from 10 randomly selected containers. These samples are analyzed for all the target analytes. The standard deviation, *s,* is calculated for each of the nine VOCs in Module IV, Table IV.D.1. The value of *n* is determined as the largest number of samples (not to exceed the number of containers in the waste stream or waste stream lot) calculated using the following equation:

$$n_{voc_i} = \frac{t^2_{0.9,n-1} s^2_{e_{voc_i}}}{E^2_{voc_i}} \qquad \text{(B2-8)}$$

Where:

n_{voci} is the number of samples needed to representatively sample the waste stream for the VOC $_i$ from Table IV.D.1
s_{evoci} is the estimated standard deviation, based on the initial 10-samples, for VOC $_i$ from Table IV.D.1
E_{voci} is the allowable error determined as 1 percent of the limiting concentration for VOC $_i$ from Table IV.D.1

Waste container samples from the preliminary mean and variance estimates may be counted as part of the total number of calculated required samples if and only if:

- There is documented evidence that the waste containers for the preliminary estimate samples were selected in the same random manner as is chosen for the required samples.
- There is documented evidence that the method of sample collection in the preliminary estimate samples were identical to the methodology to be employed for the required samples.
- There is documented evidence that the method of sample analysis in the preliminary estimate samples were identical to the analytical methodology employed for the required samples.
- There is documented evidence that the validation of the sample analyses in the preliminary estimate samples were comparable to the validation employed for the

required samples. In addition, the validated samples results shall indicate that all sample results were valid according to the analytical methodology.

The mean and standard deviation calculated after sampling *n* containers can be used to calculate a UCL_{90} for each of the headspace gas VOCs using the methodology presented in Section B2-3b.

B2-3 Upper Confidence Limits for Statistical Sampling

B2-3a Upper Confidence Limit for Statistical Solid Sampling

Upon completion of the required sampling, final mean and variance estimates and the UCL_{90} for the mean concentration for each contaminant shall be determined. The observed sample *n** shall be checked against the preliminary estimate for the number of samples (n) to be collected before proceeding, where n* is:

$$n^{*} = \frac{t^{2}_{\alpha,n-1} s^{2}}{(RT - \bar{x})^{2}} \qquad \text{(B2-9)}$$

If the observed sample *n** estimate results in greater than 20 percent more required samples than were originally calculated, then the additional samples required to fulfill the revised sample estimate shall be collected and analyzed. The determination of *n** is an iterative process that continues until the difference between *n** and the previous sample determination is less than 20 percent.

Once sufficient sampling and analysis has occurred, the waste characterization will proceed. The assessment will be made with 90 percent confidence. The UCL_{90} for the mean concentration of each contaminant will be calculated in accordance with the following equation:

$$UCL_{90} = \bar{x} + \frac{t_{\alpha,n-1} s}{\sqrt{n}} \qquad \text{(B2-10)}$$

When composite headspace gas sample results are used, the mean, standard deviation and t-statistic are based on the number of composite samples analyzed, rather than the number of drums sampled. If the UCL_{90} for the mean concentration is less than the regulatory threshold limit, the waste stream will not be assigned the hazardous waste code for this contaminant. If the UCL_{90} is greater than or equal to the regulatory threshold limit, the waste stream will be assigned the hazardous waste code for this contaminant.

B2-3b Upper Confidence Limit for Statistical Headspace Gas Sampling

If a waste stream meets the conditions for representative headspace gas sampling in Attachment B, Section B-3a(1), a UCL_{90} concentration for each of the headspace gas VOCs must be calculated from the sample data collected. The observed sample n^* shall be checked against the estimate for the number of samples (n) to be collected before proceeding, where n* is:

$$n^* = \frac{t^2_{a,n-1} s^2}{E^2} \qquad \text{(B2-11)}$$

If the observed sample n^* estimate results in greater than 20 percent more required samples than were originally calculated, then the additional samples required to fulfill the revised sample estimate shall be collected and analyzed. The determination of n^* is an iterative process that continues until the difference between n^* and the previous sample determination is less than 20 percent. Then, the UCL_{90} is calculated using equation B2-10. In this case, UCL_{90} is the 90 percent upper confidence VOC concentration, $\bar{x}$ is the calculated mean VOC concentration and s is the standard deviation. The value of $t_{(a,n-1)}$ is taken from Table 9-2 of Chapter 9 of SW-846. The calculated UCL_{90} concentration for each headspace gas VOC will then be assigned to those containers in the waste stream not selected for headspace gas sampling. If the calculated UCL_{90} concentration is less than the applicable MDL, the MDL for the VOC will be assigned to each unsampled container instead of the UCL_{90} concentration.

B2-4 Control Charting for Newly Generated Waste Stream Sampling

For newly generated waste streams that the generator characterizes using control charts, significant process changes and process fluctuations associated with newly generated waste will be determined using statistical process control (**SPC**) charting techniques; these techniques require historical data for determining limits for indicator species, and subsequent periodic sampling to assess process behavior relative to historical limits. SPC will be performed on waste prior to solidification or packaging for ease of sampling. If the limits are exceeded for any toxicity characteristic parameter, the waste stream shall be recharacterized, and the characterization shall be performed according to procedures required in the WAP.

A Shewhart control chart (Gilbert, 1987) is a control chart for means that can be used for checking whether current data are consistent with past data and whether shifts or trends in means have occurred. The control chart for means is constructed of a center line and upper and lower control limits that are based on the mean and standard deviation of historical data for the process. If a current sample mean from the process lies within the limits, the process is said to be “in control”, or consistent with historical data. If the current mean exceeds the limits, the process has likely changed from historical periods.

Logical sets of historical data to be used for the construction of limits in this application are the data from the initial characterization of the waste stream, if available, from characterization of a different lot of the waste stream, or from a retrievably stored waste stream of the same type from the same process. At a minimum, the logical set shall include ten representative sample values collected and analyzed from the newly generated waste stream. The data used for construction of the limits shall be justified. The underlying assumptions for control charts are that the data are independent and normally distributed with constant mean µ and constant variance s^2. The statistical tests for normality shall be conducted and data transformation to normality performed, if necessary. Transformations shall take place prior to any calculations that use the data.

Each limit will be constructed such that there is a 90 percent confidence that the true mean does not exceed a limit. One-sided control limits are used because once a waste stream has been determined to be RCRA-hazardous, the limit exceedance of interest is on the lower side; that is when the process may become nonhazardous. Likewise, once a waste stream has been determined not to be RCRA-hazardous, the limit exceedance of interest is on the upper side; that is when the process may become RCRA-hazardous. Whether or not exceeding the limit would result in a change in the RCRA-hazardous nature of the waste stream depends on how close the observed control limits are to RCRA limits.

Current process data will be collected and averaged for comparison to the control limit for the mean. The collection period and number of samples to be included in the average are dependent on the waste stream characteristics. A small number of samples will reflect more of the process variability and there will potentially be more limit exceedance. If two or three samples are collected for the mean in the required annual (or batch) sampling of a relatively homogeneous waste stream, limit exceedances may not occur. If the waste stream is less homogeneous, it will be necessary to collect more samples to meet the required confidence limit.

Periodically it will be necessary to update the control limit for a process. An update is performed that includes all historical data if there is no evidence of a trend in the process or a shift in the mean for the process. If there has been a shift in the mean, only more recent data that reflects the shift is used. Control limits shall be based on at least ten data points that are representative of the process and do not exhibit outliers or a trend with time.

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TABLES

TABLE B2-1
NUMBER OF WASTE CONTAINERS REQUIRING VISUAL EXAMINATION

Annual Number of Waste Containers per Summary Category Group Undergoing Characterization	Number of Waste Containers Requiring Visual Examination Based on Percent of Waste Containers Miscertified to WIPP-WAC by Radiography in Previous Year(s)													
	1% or less	2%	3%	4%	5%	6%	7%	8%	9%	10%	11%	12%	13%	14% or greater
50 or less	22[a]	22	22[a]	22	29[a]	29	41[a]	41	46[a]	46	50[a]	50	50[a]	50
100	15	24	24	33	33	41	48	62	69	81	87	96	100	100
200	15	26	26	35	44	52	68	83	105	126	152	176	196	200
300	15	26	26	35	44	53	70	94	116	153	202	247	287	300
400	15	26	26	36	45	62	79	103	134	178	235	316	377	400
500	16	26	26	36	45	63	80	104	143	196	268	364	465	500
1000	16	27	27	36	46	64	81	114	162	239	359	568	848	1000
1500	16	27	27	37	46	64	81	123	171	257	416	701	1176	1500
2000	16	27	27	37	46	64	90	123	172	266	441	795	1453	2000

[a] Number of containers for the higher even-number percent of miscertified containers is used because an odd percent implies a noninteger number of containers are likely to be miscertified.

FIGURES

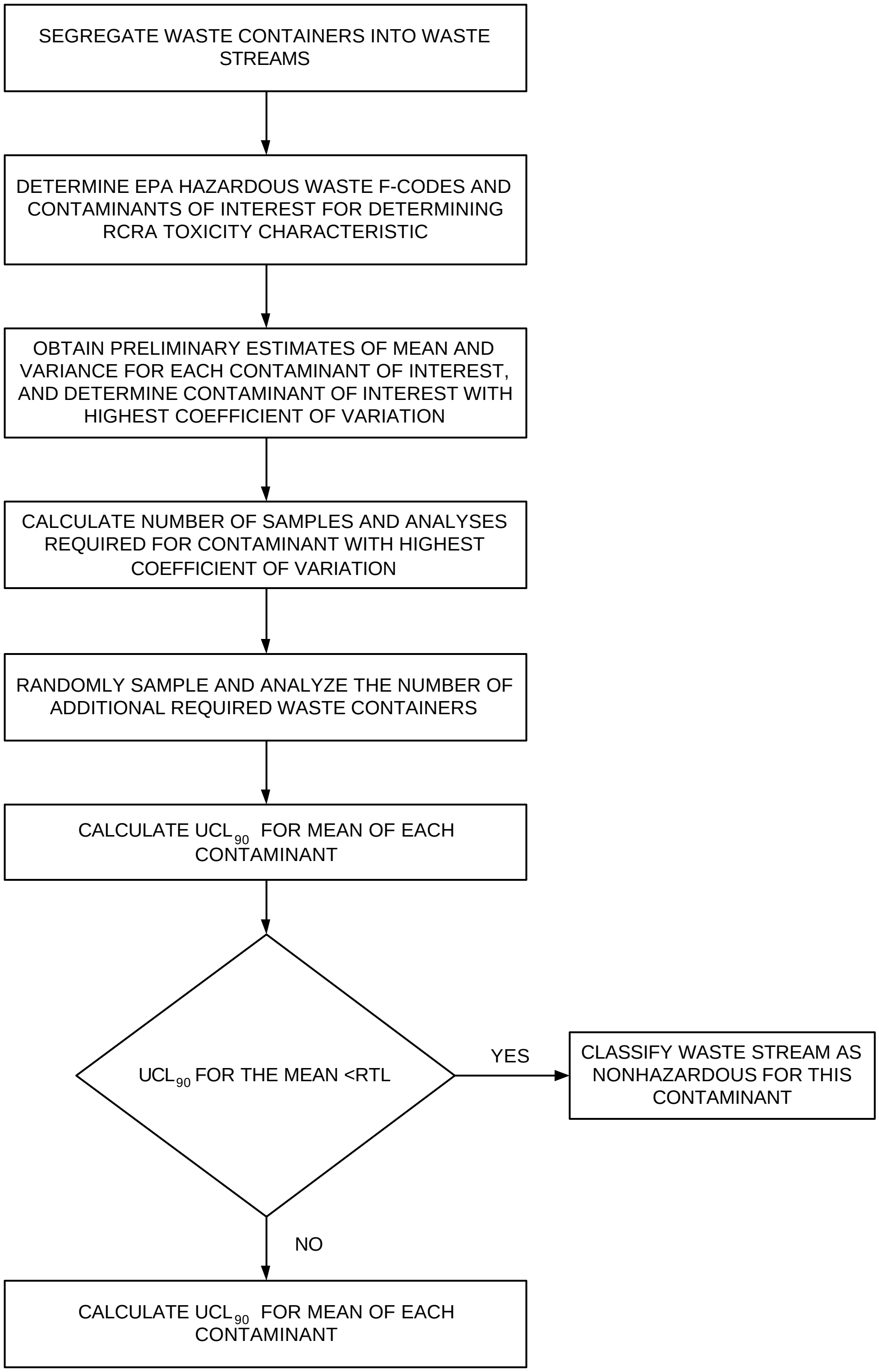

Figure B2-1
Statistical Approach to Sampling and Analysis of Waste Streams of Retrievably Stored Homogeneous Solids and Solid/Gravel